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High pressure equation of state for MgS crystal

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Abstract : A semi-empirical and semi-phenomenological equation of state is developed on the basis of interionic potential function The equation of state thus formulated is found to present remarkably close agreement with recent experimental pressure-volume data on MgS for the entire range of pressure upto 54 GPa

Keywords : Equation of state, pressure volume relationship, MgS crystal

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Recently, Peiris *et al* [1] have reported the experimental compression data for MgS (Bl or NaCl structure) for a considerably higher pressure range upto a pressure of 54 GPa (540 kbar). By fitting the Birch-Murnaghan equation of state [2] and the universal equation of state [3] to the data on MgS, they obtained the values of bulk modulus (K_0) and its first pressure derivative (K_0') at zero pressure. Values of K_0 and K_0' thus obtained from the two equations are nearly same. However, when they applied the Born model, the data could be interpreted only by reducing the ionic charges very significantly [1]. The effective charge parameter Z turned out to be 1.56 in place of its normal value 2. It should be emphasized here that the most remarkable success of the Born model has been to produce agreement with the experimental values of cohesive energies using normal values of ionic charges for a large number of ionic crystals including alkaline earth chakogenides [4–6]. Since the ionic charge appears as Z^2 in the Madelung term of the expression of cohesive energy and the major contribution to the cohesive energy arises from this term, $Z = 1.56$ in place of 2 would reduce the magnitude of cohesive energy by about 40%. This will obviously lead to a large discrepancy between calculated and experimental values of cohesive energy based on thermodynamic data.

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In the present study, we develop an equation of state on the basis of lattice potential energy W by expressing it as a function of volume in the following form [7]

$$W = -\frac{Ae^2}{V^{1/3}} + \frac{B}{V^{n/3}}, \tag{1}$$

where A, B and n are the potential parameters. The first term represents the long range electrostatic Madelung energy and the last term is the short range overlap repulsive energy. The equation of state representing the pressure volume relationship is derived from the following equation [8]

$$P = -\frac{dW}{dV}. \tag{2}$$

Eqs. (1) and (2) yield

$$P = -\frac{1}{3}\frac{Ae^2}{V_o^{4/3}}\left(\frac{V}{V_o}\right)^{-4/3} + \frac{n}{3}\frac{B}{V_0^{(n+3)/3}}\left(\frac{V}{V_o}\right)^{-(n+3)/3}, \tag{3}$$

where V_o is the volume at zero pressure. Thus applying the condition $V = V_o$ at $P = 0$, eq. (3) gives

$$B = \frac{Ae^2 V_o^{(n-1)/3}}{n}. \tag{4}$$

With the help of eqs. (3) and (4) we obtain

$$P = -\frac{Ae^2}{3V_o^{4/3}}\left[\left(\frac{V}{V_o}\right)^{-4/3} - \left(\frac{V}{V_o}\right)^{-(n+3)/3}\right]. \tag{5}$$

The expressions for K_o and K_o' are also obtained as follows using the method described earlier [7].

$$K_o = \frac{Ae^2(n-1)}{9V_o^{4/3}} \tag{6}$$

and

$$K_o' = \frac{n+7}{3}. \tag{7}$$

Now, we adopt the semi-empirical and semi-phenomenological methods for determining the potential parameters. Recent studies on high pressure behaviour of ionic solids, have extensively used the approximation $K_o' = 4$ [1,9,10]. We therefore, take the Born exponent $n = 5$ so as to yield $K_o' = 4$ with the help of eq. (7). Value of A is determined to be 8.2 taking the experimental value $V/V_0 = 0.9778$ at $P = 1.8$ GPa. Eq. (5) is then used to evaluate pressures taking particular values of V/V_0 as listed by Peiris *et al* [1]. The results are reported in Table 1. It is indeed impressive to observe from Table 1 that the calculated values of P agree remarkably well with the compression data within experimental uncertainties for the entire range.

Table 1. Values of pressure calculated from eq. (5) for MgS

V/V_0 (used as input)	P (GPa)	
	Calculated	Experimental [1]
0.9778	1.8	1.8 ± 0.2
0.9532	4.1	4.5 ± 0.2
0.9138	8.2	8.0 ± 0.9
0.9127	8.4	8.8 ± 1.2
0.8816	12.4	12.4 ± 0.5
0.8483	17.5	15.9 ± 3.7
0.8451	18.1	17.3 ± 0.8
0.8210	22.5	21.8 ± 1.0
0.7988	27.1	26.0 ± 1.4
0.7898	29.1	26.6 ± 4.5
0.7788	31.7	30.3 ± 3.6
0.7794	31.6	30.9 ± 1.5
0.7557	37.8	35.9 ± 4.4
0.7616	36.7	36.5 ± 1.9
0.7508	39.2	39.3 ± 2.3
0.7308	45.3	43.1 ± 3.8
0.7327	44.7	44.1 ± 2.8
0.7130	51.4	46.9 ± 5.6
0.7183	49.5	50.7 ± 3.0
0.7098	52.6	53.3 ± 3.8
0.7036	54.9	54.3 ± 6.5

It is pertinent to compare here the Madulung term in the present analysis with the corresponding term in the original Born model. Thus we have

$$\frac{Ae^2}{V_0^{1/3}} = -\alpha_M \cdot \frac{Z^2e^2}{r_0} \tag{8}$$

where e is the electron charge and r_0 is the equilibrium nearest neighbour interionic separation. In view of the relation $V_0 = 2r_0^3$ for NaCl structure, we can evaluate Z with the help of eq. (8) taking $A = 8.2$ and $\alpha_M = 1.74756$. We thus find $Z = 1.93$ in place of its normal value ($Z = 2$). Such a small reduction (3 or 4%) in the value of ionic charge is consistent with a wide variety of data on cohesive energy, elastic constants and dielectric constants for ionic solids [11,12]. Finally, we have also calculated the value of K_0 for MgS with the help of eq. (6) which turns out to be 76.6 GPa in close agreement with the value 78.9 ± 3.7 GPa reported by Peiris *et al* [1]. To conclude, the analysis presented here is consistent with the data on high-pressure behaviour of MgS.

References

[1] S M Peiris, A J Campbell and D L Heinz *J. Phys Chem Solids* **55** 413 (1994)

[2] F Birch *J Geophys. Res* **83** 1257 (1978)

[3] P Vinet, J Ferrante, J H Rose and J R Smith *J. Geophys. Res.* **92** 9319 (1987)

[4] M L Huggins and Y Sakamoto *J. Phys. Soc. Jpn* **12** 241 (1957)

[5] M Catti *Solid State Commun.* **29** 243 (1979)

[6] S D Chaturvedi, S B Sharma, P Paliwal and M Kumar *Phys. Stat. Sol* (b) **156** 171 (1989)

[7] R Jayaprakash, S S Kushwaha and J Shanker *Physica* **C227** 109 (1994)

[8] M P Tosi *Solid State Phys.* **16** 1 (1964)

[9] A J Campbell and D L Heinz *J Phys Chem Solids* **52** 495 (1991)

[10] X Xia and J K Xiao *J. Phys Chem Solids* **54** 629 (1993)

[11] M J L Sangster, U Schroder and R M Atwood *J Phys* **C11** 1523, 1541 (1978)

[12] J Shanker and S Dixit *Phys Stat Sol* (a) **123** 17 (1991)